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March 13, 2006

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APPLICATION NUMBER: *60/647,589*
FILING DATE: *January 27, 2005*
RELATED PCT APPLICATION NUMBER: *PCT/US06/03152*

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS *US60/647,589*

Certified by

Jon W. Dudas

Under Secretary of Commerce
for Intellectual Property
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. EV 534972848 US

INVENTOR(S)		
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Csaba	Szeles	Allison Park, Pennsylvania
Vincent D.	Mattera, Jr.	Gibsonia, Pennsylvania
Scott E.	Cameron	Lower Burrell, Pennsylvania

Additional inventors are being named on the _____ *separately numbered sheets attached hereto*

TITLE OF THE INVENTION (500 characters max):

"DOPING RECIPE FOR SEMI-INSULATING $Cd_xZn_{(1-x)}Te$ ($0 \leq x \leq 1$) FOR RADIATION DETECTOR APPLICATIONS"

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

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ENCLOSED APPLICATION PARTS ***(check all that apply)***

[ ] Application Data Sheet. See 37 CFR 1.76
[ ] CD(s), Number of CDs _____
[X] Specification *Number of Pages* 6
[ ] Other (specify) _____
[X] Drawing(s) *Number of Sheets* 1

Application Size Fee: If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

METHOD OF PAYMENT OF FILING FEES AND APPLICATION SIZE FEE FOR THIS PROVISIONAL APPLICATION FOR PATENT

[ ] Applicant claims small entity status. See 37 CFR 1.27.
[X] A check or money order is enclosed to cover the filing fee and application size fee (if applicable).
[ ] Payment by credit card. Form PTO-2038 is attached.
[X] The Director is hereby authorized to charge the filing fee and application size fee (if applicable) or credit any overpayment to Deposit Account Number: 23-0650. A duplicative copy of this form is enclosed for fee processing.

TOTAL FEE AMOUNT ($): $200.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

[X] No.
[ ] Yes, the name of the U.S. Government agency and the Government contract number are: _____

SIGNATURE Richard L. Byrne Date January 27, 2005

TYPED or PRINTED NAME Richard L. Byrne REGISTRATION NO. 28,498 *(if appropriate)*

TELEPHONE 412-471-8815 Docket Number: 4375-050273

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT.

Effective on 12/08/2004.
Fees pursuant to the Consolidated Appropriations Act, 2005 (H.R. 4818)

FEE TRANSMITTAL For FY 2005

☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT ($200.00)

Complete if Known	
Application Number	Not Yet Assigned
Filing Date	Concurrently Herewith
First Named Inventor	Csaba Szeles et al.
Examiner Name	Not Yet Assigned
Art Unit	Not Yet Assigned
Attorney Docket No.	4375-050273

METHOD OF PAYMENT (check all that apply)

[X] Check [ ] Credit Card [ ] Money Order [ ] None [ ] Other (please identify): _____

[X] Deposit Account Deposit Account Number: 23-0650 Deposit Account Name _____

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FEE CALCULATION

1. BASIC FILING, SEARCH, AND EXAMINATION FEES

	FILING FEES		SEARCH FEES		EXAMINATION FEES		
		Small Entity		Small Entity		Small Entity	
Application Type	Fee ($)	Fee ($)	Fee ($)	Fee ($)	Fee ($)	Fee ($)	Fees Paid ($)
Utility	300	150	500	250	200	100	
Design	200	100	100	50	130	65	
Plant	200	100	300	150	160	80	
Reissue	300	150	500	250	600	300	
Provisional	200	100	0	0	0	0	$200.00

2. EXCESS CLAIM FEES

Fee Description	Fee ($)	Small Entity Fee ($)
Each claim over 20 or, for Reissues, each claim over 20 and more than in the original patent	50	25
Each independent claim over 3 or, for Reissues, each independent claim more than in the original patent	200	100
Multiple dependent claims	360	180

Total Claims		Extra Claims	Fee ($)		Fee Paid ($)
_____	- 20 or HP =	_____	x _____	=	_____

HP = highest number of total claims paid for, if greater than 20

Multiple Dependent Claims	
Fee ($)	Fee Paid ($)
_____	_____

Indep. Claims		Extra Claims	Fee ($)		Fee Paid ($)
_____	- 3 or HP =	_____	x _____	=	_____

HP = highest number of independent claims paid for, if greater than 3

3. APPLICATION SIZE FEE

If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

Total Sheets		Extra Sheets		Number of each additional 50 or fraction thereof		Fee ($)		Fee Paid ($)
28	- 100 =	_____	/ 50 =	_____	(round up to a whole number) x	_____	=	_____

4. OTHER FEE(S)

	Fee Paid ($)
Non-English Specification, $130 fee (no small entity discount)	_____
Other: _____	_____

SUBMITTED BY

Signature	Richard L. Byrne	Registration No. (Attorney/Agent) 28,498	Telephone 412-471-8815
Name (Print/Type)	Richard L. Byrne		Date January 27, 2005

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:	ATTORNEY'S DOCKET NUMBER
CSABA SZELES, VINCENT D. MATTERA, JR. and SCOTT E. CAMERON	**4375-050273**

ENTITLED

"DOPING RECIPE FOR SEMI-INSULATING $Cd_xZn_{(1-x)}Te$ ($0 \leq x \leq 1$) FOR RADIATION DETECTOR APPLICATIONS"

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

EXPRESS MAIL CERTIFICATE

"Express Mail" Label Number **EV 534972848 US**

Date of Deposit January 27, 2005

I hereby certify that the following attached paper(s) and/or fee(s):

FEE TRANSMITTAL (1 p. – in trip.);
PROVISIONAL APPLICATION COVER SHEET (1 p. – in trip.);
SPECIFICATION (6 pp.);
DRAWINGS (1 sheet);
RECORDATION FORM COVER SHEET (1 p.);
ASSIGNMENT (1 p); and
CHECKS in the amounts of $200.00 & $40.00.

are being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. §1.10 on the date indicated above and are addressed to the Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Deborah L. Hartmann
(Typed name of person mailing paper or fee)

Deborah L. Hartmann
(Signature of person mailing paper or fee)

DOPING RECIPE FOR SEMI-INSULATING $Cd_xZn_{(1-x)}Te$ ($0 \leq x \leq 1$) FOR RADIATION DETECTOR APPLICATIONS

DESCRIPTION OF THE INVENTION

[0001] This patent disclosure describes a new approach to obtain semi-insulating low-defect density cadmium telluride (CdTe) and cadmium zinc telluride (CdZnTe) crystals for X-ray and gamma ray radiation detector applications. Although, the invention is described for semi-insulating $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) for radiation detector applications the principal techniques apply to obtain any II-VI compound with semi-insulating properties. As such the technique is applicable to any nonlinear or electro-optical device or application where semi insulating or high resistivity semiconductor material is required. The $0 \leq x \leq 1$ concentration or mole fraction range encompasses CdZnTe with any Zn percentage including CdTe ($x = 0$) and ZnTe ($x = 1$).

[0002] Two fundamental physical properties govern the selection of materials for X-ray and gamma-ray radiation detector applications: first, the material must exhibit high electrical resistivity (the material is semi insulating), and second, the material must exhibit an excellent transport of charge carriers generated by the external X-ray or gamma-ray radiation (low density of defects trapping the charge carriers). None of these properties are exhibited by high-purity intrinsic (i.e. undoped) $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$). Incorporation of residual impurities and the formation of native defects render intrinsic $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) low resistivity and exhibit strong carrier trapping at the crystal defects that hamper carrier transport and radiation detection performance.

[0003] In this invention we describe a process where specific combination of impurity atoms in specific quantities are introduced to $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) in a controlled way to reliably produce extrinsic (i.e. doped) $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) with high resistivity (semi-insulating) and excellent carrier transport properties. In the process (referred to as "co-doping") two different impurities (dopants) are deliberately incorporated to the CdZnTe crystals during the crystal growth process to obtain $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) with the desired resistivity and carrier transport properties. In this co-doping scheme elements from column III of the periodic table, boron (B), aluminum (Al), gallium (Ga), indium (In) or thallium (Tl) or elements from column VII of the periodic

table, fluorine (F), chlorine (Cl), bromine (Br) or iodine (I) are introduced in the 10 atomic parts per billion (ppb) to 10000 atomic parts per billion concentration range (10 – 10000 at ppb) in parallel with the element Ruthenium (Ru) in the 10 atomic parts per billion (ppb) to 10000 atomic parts per billion concentration range (10 – 10000 at ppb). The indicated dopant concentrations are those measured by Glow Discharge Mass Spectroscopy (GDMS) in the resulting $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) crystals. The resulting $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) crystals are referred to as co-doped by X-Y, where X equals any of the elements B, Al, Ga, In, Tl, F, Cl, Br, I and Y equals the element Ru (i.e. co-doping by Al-Ru, In-Ru, Cl-Ru etc).

[0004] The described co-doping technique works on the principle of electrical compensation. Intrinsic (undoped) $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) is typically rendered low resistivity due to doping by the uncontrolled amount of residual impurities and native defects such as cadmium vacancies incorporated to the material during crystal growth. These crystal defects are ionized at ambient temperature and provide ample supply of free charge carriers (electrons or holes) resulting in conductive or low resistivity $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$). The concentration of free charge carriers in these undoped crystals is typically proportional to the concentration of the defects of their origin. The defects also trap the charge carriers generated by the external X-ray or gamma-ray radiation limiting their transport and the use of the material in radiation detector devices.

[0005] In intrinsic $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) cadmium vacancies (vacant lattice sites) are generally considered as the dominant native defects that supply high concentration of holes to the valence band of the $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) and render the material p-type (conductivity type due to holes) with resistivity in the 1 to 10^7 Ohm-cm range. This typical resistivity of intrinsic $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) is at least 3 orders of magnitude lower than the maximum resistivity, $\geq 1\times10^{10}$ Ohm-cm, achievable in this material. Defects and impurities that produce free holes are referred as acceptors.

[0006] By the deliberate introduction of impurities that produce charge carriers of the opposite sign (i.e. electrons) the phenomenon of electrical compensation can be achieved. Defects and impurities providing free electrons to the crystals are referred to as donors. By the introduction of dopants of the opposite sign, the effect of the original dopants can be compensated. As a result the concentration of the free charge carriers is now

proportional to the difference of the concentrations of acceptor and donor defects. In $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) the column III impurities (B, Al, Ga, In, Tl) and the column VII impurities (F, Cl, Br, I) serve as donors and can be used to compensate the effect of acceptors such as cadmium vacancies. The net carrier concentration equals the difference of the concentration of the column III or column VII impurity and the concentration of the cadmium vacancies. In this process the net carrier concentration is typically reduced by 2 to 6 orders of magnitude. It is, however, very difficult to reliably control the exact concentration of acceptor and donor defects and to achieve fully compensated (i.e. high resistivity $\geq 1\times10^{10}$ Ohm-cm) material. Typically resistivity in the $1\times10^{6} - 1\times10^{9}$ Ohm-cm range is achieved by column III or column VII impurity doping in $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$).

[0007] In this invention we deliberately introduce a second doping impurity in parallel with the column III or column VII impurity during the growth process of $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) to achieve full electrical compensation and high-resistivity (semi-insulating) material. By the introduction of the second doping impurity, which exhibits an energy level close to the middle of the band gap of $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) i.e. Ruthenium (Ru) in parallel with the column III or column VII dopant fully compensated material is obtained. The impurity atoms with defect levels close to the middle of the band gap are called deep dopants (deep donors and acceptors). With this procedure semi-insulating $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) with electrical resistivity exceeding $\geq 1\times10^{10}$ Ohm-cm is reliably and reproducibly achieved. In this process the additional deep dopant (i.e. Ru) electrically compensates the residual charge carriers given by the difference of the concentrations of acceptors (i.e. cadmium vacancies) and donors (i.e. column III or column VII impurities). By the introduction of Ru in sufficient concentration the concentration of these deep defects dominate over the residual carrier concentration from the direct compensation between acceptors and donors. The residual carriers will reside at the deep defect levels and no free carriers remain to facilitate electrical conduction. As a result, fully compensated $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) with resistivity at the theoretical maximum value is reliably achieved.

[0008] In addition to electrically compensating the acceptors (i.e. cadmium vacancies), column III or column VII impurities also combine with the cadmium

vacancies to form impurity-vacancy pairs commonly known as A-centers. In this process which is often called passivation the energy level of the cadmium vacancy defect is shifted to the lower energy level of the A center. The lower energy of the new defect (A center) reduces the residency time of charge carriers (holes) at the defect and increases the transport properties of carriers generated by the external X-ray and gamma-ray radiation. As a result the performance of radiation detector devices fabricated from the co-doped, $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) crystals are greatly improved.

[0009] The use of two dopants in parallel (co-doping) also enables the use of the low concentrations of individual dopants to achieve full compensation. This eliminates the adverse effects of single doping schemes using massive concentrations of dopants on the carrier transport properties of $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$).

[0010] Semi-insulating $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) crystals are typically grown from melt by the Bridgman, gradient freeze, electrodynamic gradient techniques or by vapor phase transport. The growth can be implemented in any of these techniques in a high-pressure or low pressure mode and either in the horizontal or vertical configuration. Also in any of these techniques the growth can be performed with or without the partial pressure control of the crystal components (Cd, Zn and Te). The discussed invention pertains to co-doping in any crystal growth process.

[0011] With reference to Fig. 1, once a $Cd_xZn_{1-x}Te$ ($0 \leq x \leq 1$) crystal including the co-doping scheme discussed above has been formed into an ingot, a slice or wafer 2 of the crystal is removed therefrom. Wafer 2 can then be formed into a pixilated array where each picture element or pixel 4 is capable of converting incident radiation, such as x-rays and gamma rays, or incident particles, such as alpha or beta particles, into an electrical signal independent of every other pixel 4 of the array. Alternatively, wafer 2 can be a crystal that outputs an electrical signal in response to incident radiation or an incident particle, but which does not include a plurality of individual pixels 4. An example of wafer 2 including a single pixel 4 isolated from the reminder of wafer 2 is shown in Fig. 1. However, this is not to be construed as limiting the invention since a planar crystal can be formed in any desired and manufacturable size and shape.

[0012] The invention has been described with reference to the preferred embodiment. Obvious modifications and alterations will occur to others upon reading and

understanding the preceding detailed description. It is intended that the invention be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

THE INVENTION IS CLAIMED TO BE:

1. A radiation detector made from a compound comprising:

$Cd_xZn_{1-x}Te$, where $0 \leq x \leq 1$;

an element from column III or column VII of the periodic table in a concentration about 10 to 10,000 atomic parts per billion; and

the element Ruthenium (Ru) in a concentration about 10 to 10,000 atomic parts per billion.

2. A method of forming a radiation detector compound comprising:

(a) providing a mixture of Cd, Zn and Te;

(b) heating the mixture to a liquid state;

(c) adding to the liquid mixture a first dopant that adds shallow level donors (electrons) to the top of an energy band gap of said mixture when it is solidified;

(d) adding to the liquid mixture a second dopant that adds deep level donors and/or acceptors to the middle of said band gap of said mixture when it is solidified; and

(e) solidifying said mixture including said first and second dopants to form the compound, wherein the second dopant is the element Ruthenium (Ru).

3. The method of claim 2, wherein the first dopant is an element from column III or column VII of the periodic table.

4. The method of claim 3, wherein the first dopant is an element selected from the group consisting of B, Al, Ga, In, Tl, F, Cl, Br and I.

5. The method of claim 2, wherein a concentration of the first dopant in the compound is about 10 to 10,000 atomic parts per billion.

6. The method of claim 2, wherein a concentration of the element Ruthenium (Ru) in the compound is about 10 to 10,000 atomic parts per billion.